Consolidating Molecular Logic with New Solid-bound YES and PASS 1 Gates and their Combinations

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Bernadine O. F. McKinney, Brian Daly, Chaoyi Yao, Marc Schroeder, and A. Prasanna de Silva*[a]

Abstract: H^+-driven YES and PASS 1 molecular logic tags based on anthracene and 4-aminonaphthalimide fluorophores emitting blue and green, respectively, are employed on amino-terminated polyethyleneglycol-polystyrene and aminopropyl silica particles. The (YES + PASS 1) logic combination is also a distinguishable tag in both colours. The scope of such tags is delineated.

Introduction

Following humble beginnings,[1] molecular logic-based computation is now in a phase of consolidation as evidenced by 500 laboratories contributing to the movement (Figure 1). Additional evidence of this consolidation can be found in a dedicated conference series,[2] a real-life medical application,[3] a number of dedicated books and reviews,[4] besides sections of others[5] and several dedicated special issues and article collections such as this one.[6] Other evidences are the extension of Boolean principles to molecular versions of arithmetic,[7] ID tagging,[8] cryptography,[9] arrayed logic,[10] in situ imaging,[11] conditional photodynamic therapy,[12] intracellular logic,[13] multi-valued logic,[8,14] human-level computing,[15] among others. Extending the principles learned with molecules in solution to those on solids would be one general avenue of this consolidation scenario. The current work takes some steps in this direction.

Transplanting molecular logic onto solids might appear counter-productive at first sight, since the solid object tends to be far larger than the molecular device so that space-resolution is sacrificed. A strength of molecular logic devices is their small size (1-2 nm) while operating wirelessly. In comparison, semiconductor logic devices, with associated wires or antennas for human interfacing, remain substantially larger.[16] Nevertheless, molecules on solids open up another horizon: that of attaching tiny logic tags to identify larger objects within a population.[8] It has even been suggested that the larger object could be a large molecule.[17] While recognizing that the PASS 0 logic case is embedded within tag-free objects,[8] the current work explores new tag-solid constructs which are based on the simplest Boolean operations: PASS 1 and YES logic. The fluorescence intensity output of the H^+-driven YES gate is 'high' when the H^+ concentration is 'high'. Its output is 'low' when the H^+ level is 'low'. The fluorescence output of the H^+-driven PASS 1 gate is 'high' irrespective of the H^+ level. Conversely, H^+-driven PASS 0 gates show no fluorescence whatever the H^+ level.

Figure 1. Approximate world maps of the sources of molecular logic devices. Only the names of corresponding authors from the literature are given. Single input - single output devices have been omitted.

The first molecular logic tags were H^+-driven YES gate **1** and PASS 1 gate **2** covalently bound to amino-terminated polyethyleneglycol-polystyrene (APEG-PS) beads (average diameter ~100 μm).[8] We now present new data on these and related new systems in order to better understand the scope of molecular computational identification[8] (MCID). The initial logic-tagged objects **3** and **4** consisted of an organic polymer particle and a blue-emitting hydrocarbon

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fluorophore with a more-or-less pure ππ* excited state[8] (Figure 2). Logically, at least two avenues open up for extending the MCID concept. First, inorganic polymer particles such as aminopropylsilica (APS)[18] deserve attention. Second, heteroaromatic fluorophores with internal charge transfer (ICT) excited states,[19,20] e.g. green-emitting 4-aminonaphthalimide[21] will be examined. The receptor module necessary for the expression of some logic types, e.g. H^+-binding tertiary amine, is carried forward from the initial study.[8] A pyridine receptor for H^+ and a benzocrown ether receptor for Na^+ have also been used in previous studies.[8,22]

Results and Discussion

Starting materials **1** and **2** were available from the initial study.[8] These are attached to APS particles (average diameter ~50 μm) via dicyclohexylcarbodiimide-type coupling to create amide bonds and to produce **5** and **6**. The green-emitting H^+-driven PASS 1 tag **7** is easily accessible by reacting 4-chloro-1,8-naphthalic anhydride **22** with glycine t-butylester, followed by a nucleophilic aromatic substitution of the halogen by 1-butylamine and a final step of ester hydrolysis (Figure 3). A similar route, but with 2-(diethylamino)ethylamine replacing 1-butylamine in the second step, yields the green-emitting H^+-driven YES logic tag **8**. **7** and **8** are connected via amide bonds to APEG-PS and APS to produce **9**, **10**, **11** and **12**. When a more water-compatible PASS 1 logic tag became necessary, ester-protected **8**, **13**, was quaternized with iodomethane followed by ester hydrolysis. **14** and **15** are the resulting tagged polymer particles.

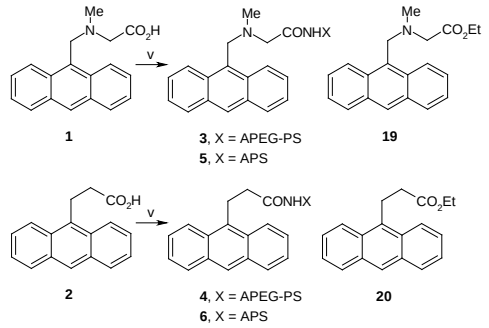

Figure 2. Chemical structures of the blue-emitting anthracene-related compounds used in this study and some of their precursors. Reagents for the conversions are given under Figure 3.

A powerful feature of logic tagging arises through non-Boolean multi-valued logic.[4] Such examples are built by double-tagging the polymer particles with **1** and **2** or with **8** and **16**. (YES + PASS 1) logic-tagged APS **17** emits blue and **18** emits green (Figure 4). Although double (or multiple)-tagging can be carried out in various tag molar ratios,[8] only 1:1 versions are studied here.

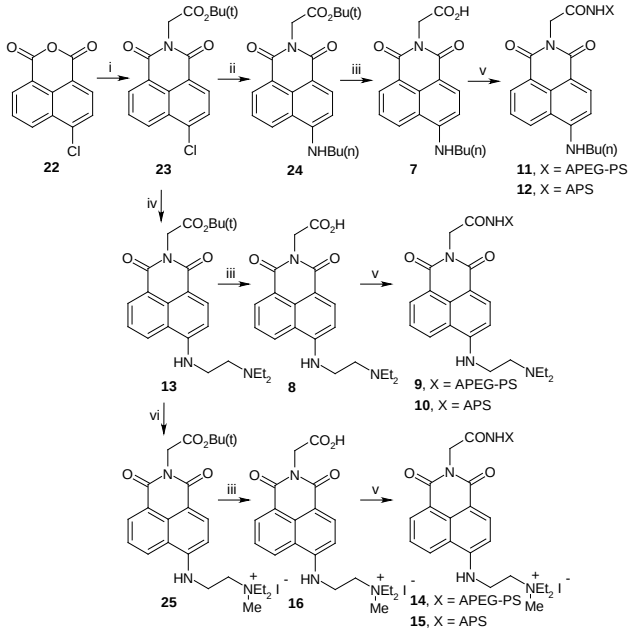

Figure 3. Chemical structures of the green-emitting 4-aminonaphthalimide-related compounds used in this study and some of their precursors. Reagents for the various conversions are; i. glycine t-butylester, ii. N-butylamine, iii. formic acid, iv. N,N-diethylaminoethylamine, v. APEG-PS or APS, Diisopropylcarbodiimide, hydroxybenzotriazole, vi. MeI.

Comparison of the emission spectra of **19**,[8] **3** and **5** at acidic pH (Figure 5) shows the occurrence of self-absorption as the anthracene fluorophores are anchored on APEG-PS and, even more so, on APS at 5% loading. The well-known smallness of the Stokes shift in ππ* emission spectra[23] leads to self-absorption of the 0-0 vibrational band of the emission spectrum and, to a lesser extent, the 0-1 band, when these fluorophores are present at a high effective local concentration. The linear and flexible PEG chains on APEG-PS spread out since they are rather well-solvated in methanol:water (1:1, v/v). Hence the fluorophores are comparatively further apart and suffer less self-absorption than that seen when they are anchored with a short propyl chain to the silica core of APS. The same trend is seen from the I_{00}/I_{02} and I_{01}/I_{02} values (Table 1) for the anthracene-based PASS 1 logic cases **20**,[8] **4** and **6**. Such self-absorption issues do not arise in the emission spectra of 4-aminonaphthalimides **7** - **12**, **14** - **16** and **18** with ICT excited states owing to their substantial Stokes shifts in polar media.[23]

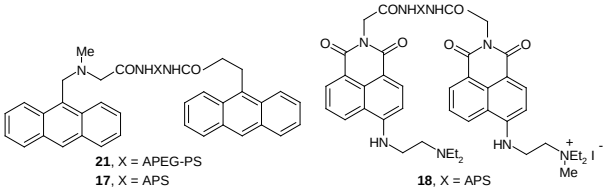

Figure 4. Chemical structures of the blue- and green-emitting (YES + PASS 1) logic tagged objects used in this study. The gate loading is 2.5% each in each case.

The fluorescence emission wavelengths due to the ππ* excited states of the anthracene-based YES gates **19**, **3** and **5** are essentially constant (Table 1) since the emissive protonated forms are hydrophilic enough to take up positions in the mixed aqueous medium further from the polymer surface. A slight ICT character induced in the anthracene excited state by the electron-withdrawing protonated aminomethyl substituent puts the wavelengths at 400, 425 and 445 nm. All corresponding wavelengths of the uncharged PASS 1 gate **20** are blue-shifted about 10 nm due to the lack of such an ICT contribution. The hydrophobic fluorophores within **4** and **6** are held close to the polymer surface and hence the observable emission wavelengths are shifted back into the range observed for the YES logic-tagged cases **3** and **5**. Such near coincidence of the 0-1 vibrational bands of polymer-bound PASS 1 and YES gates is vital for the near-ideal operation of gate combinations (see below).

Where observable, the absorption and emission wavelengths of ICT-based fluorophores within the protonated YES gates **8**, **9** and **10** are blue-shifted about 18 nm when compared to the corresponding PASS 1 logic systems **7**, **11** and **12**, due to an electrostatic destabilization of the excited state by the protonated amine two methylene groups away.[24] The more water-compatible PASS 1 logic systems **16**, **14** and **15**, which carry a quaternary ammonium centre near the fluorophore, naturally have wavelengths nearly identical to the YES gates.

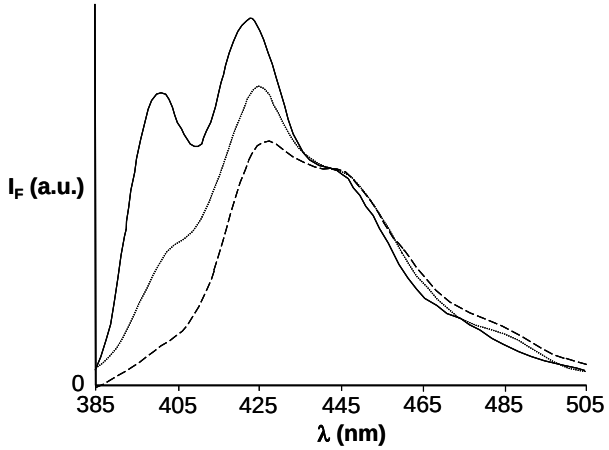

Figure 5. Fluorescence emission spectra of **19** (full line), **3** (dotted line) and **5** (dashed line) in methanol: water (1:1, v/v) at pH 2.5 and normalized at the 0-2 band maximum. The excitation wavelength is 368 nm.

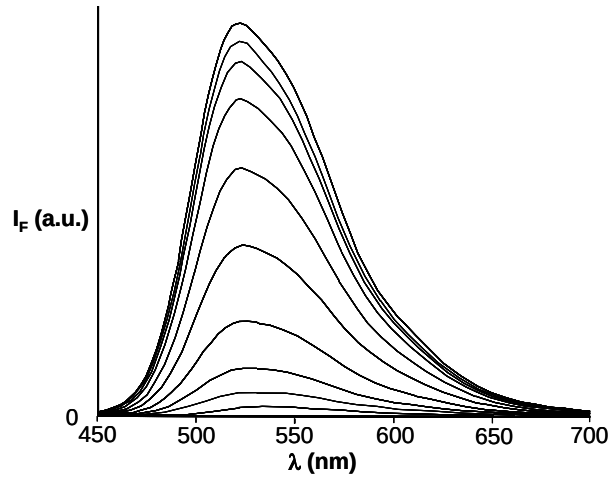

Figure 6. Family of fluorescence emission spectra of **8** in methanol:water (1:1, v/v) as a function of pH. The excitation wavelength is 432 nm. pH values in order of increasing intensity: 11.0, 10.4, 9.9, 9.4, 8.9, 8.5, 7.9, 7.5, 7.0 and 2.5.

It is clear from Figure 6 and the large H^+-induced fluorescence intensity enhancement factors (FE_{H+} values, Table 1) that excellent H^+-driven YES logic behaviour is seen in the fluorescence 'off-on' action. Aminoalkyl appended fluorescent dyes are prototypical 'fluorophore-spacer-receptor' systems[19,24-26] where photoinduced electron transfer (PET) occurs from the amino group to the fluorophore across the spacer until it is arrested by protonation of the amine. It is gratifying to see the fluorescence switching action observed for the dissolved compounds, e.g. **19** and **8**, carrying through when they are anchored at the polymer-liquid interface (e.g. **9** and **10**, Figures S1 and S2 and Table 1).

Although PET switching thermodynamics in homogeneous solution is reasonably predictable from measured redox potentials[27] or from calculated frontier orbital energies,[28] it is more difficult to assess in the polymer environment. This is specially relevant since lower polarity media are known to retard PET,[29] which would reduce the FE_{H+} values to what is observed here.

Table 1. Optical properties of the logic tags and tagged polymer particles in methanol:water (1:1, v/v).

Case	λ_{ex} (nm)	λ_{em} (nm)	I_{00}/I_{02}[a]	I_{01}/I_{02}[a]	pK_a*	g		FE_{H+}[b]
19	368	400, 425, 443	1.34	1.66	5.3	0.93		59
3	368	400, 425, 445	0.64	1.38	3.9	0.70		38
5	368	427, 445	0.16	1.08	5.2	0.45		77
20	368	390, 410, 436	1.86	2.07	n/a	n/a		1.1
4	368	401, 420, 442	0.82	1.70	n/a	n/a		1.0
6	368	419, 440	0.25	1.30	n/a	n/a		1.0
21	368	400, 420, 440	0.73	1.54	4.1	0.78		2.0[c]
17	368	422, 440	0.35	1.12	5.2	0.38		2.0[c]
8	432	525	n/a	n/a	8.7	0.75		44
9	432	523	n/a	n/a	8.2	0.62		20
10	432	529	n/a	n/a	9.7	0.48		99[d]

a; I_{00} is the emission intensity observed for the 0-0 transition etc. , b; $I_{F\ pH2.5}/I_{F\ pH11.0}$, c; Measured at λ_{em} = 422 nm, d; $I_{F\ pH2.5}/I_{F\ pH13.0}$, e; Apparent pK_a* = 8.2, f; Measured at λ_{em} = 530 nm.

The pH dependence of the fluorescence intensity (I_F) is analyzed according to a generalized version of the Henderson-Hasselbalch equation (1),

$$\log[(I_{Fmax} - I_F)/(I_F - I_{Fmin})] = g.pH - g.pK_a^* \quad (1)$$

where I_{Fmax} and I_{Fmin} are measured at pH values of 2.5 and 11.0 respectively and where g is ideally unity. Although this last condition is commonly approached in homogeneous mixed aqueous solution,[30,31] e.g. **19** and **8**, it is not obvious at polymer-liquid interfaces. Indeed, the well-solvated termini of the APEG-PS are seen to approach the conditions

7	450	549	n/a	n/a	n/a	n/a		0.9
11	450	436	n/a	n/a	n/a	n/a		1.0
12	450	547	n/a	n/a	n/a	n/a		1.0
16	429	520	n/a	n/a	n/a	n/a		1.0
14	429	525	n/a	n/a	n/a	n/a		1.6[e]
15	429	531	n/a	n/a	n/a	n/a		1.0
18	429	530	n/a	n/a	9.8	0.75		1.5[f]

prevailing in homogeneous solution with g = 0.70 for **3**. In contrast, the YES gate at the APS surface, e.g. **5**, shows a noticeably smaller g value of 0.45 (Table 1). This divergence persists in the double labeled (YES + PASS 1) logic cases **21** and **17**. Similarly, the APEG-PS YES logic case of **9** has g = 0.62 whereas the APS-bound analogue **10** only has g = 0.48. Such deviation from ideality can be understood in terms of the fluorophores being held closer to the APS surface, e.g. in **18** and in **10**, which reduces their solvation. A range of individual pK_a* values are expressed by different sub-populations of tags present in environments of varying polarities due to the restricted solvation. Different domains of tags on the polymer surfaces are also probably involved. The reduced g values indicate the widths of the pK_a* distribution.[32]

The pK_a* values also throw light on the effect of translocating the 'fluorophore-spacer-receptor' system from homogeneous mixed aqueous solution to the polymer-solution interface. The rather apolar environment created by PEG chains, as compared to methanol-water, in **3** lowers its pK_a* value to 3.9 as compared to 5.3 seen in **19**. Another contributor to this drop in pKa* is the repulsion of H^+ from the protonated amine terminals of the polymer particles.

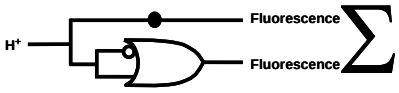

Figure 7. Physical electronic representation of (YES + PASS 1) logic. It is noted that binary logic symbols are employed as starting points to depict a ternary logic device.

Although the environment near APS is apolar too, its Si-O^- moieties electrostatically concentrate H^+ locally so that the effective pK_a* value (5.2) for **5** approaches that found in homogeneous solution. This effect dominates over the H^+ repelling effect of the partially protonated amine termini since the latter are less numerous than the Si-O^- moieties. Similar arguments hold true in the (YES + PASS 1) logic cases **21** and **17**. In the 4-aminonaphthalimide series, the APEG-PS YES logic case **9** has a pK_a* value of 8.2, which is noticeably lower than that found in homogeneous solution for **8** (8.7) due to the reduced polarity of the APEG-PS environment and the H^+ repulsion effect of the partially protonated amine termini. Again, the electrostatic effect of the Si-O^- groups raises the pK_a* value of **10** to 9.7. Such a high value suggests a more polar environment for the tag in **10** than in **5**. This is to be expected given the lower Hansch hydrophobicity[33] of 4-aminonaphthalimide as compared to anthracene.

FE_{H+} values for all the PASS 1 logic gates studied here are close to ideal value of unity, with one exception. APEG-PS particles tagged with 4-aminonaphthalimide carrying a quaternary ammonium side-chain, **14**, show a FE_{H+} value of 1.6, alongside an apparent pK_a* value of 8.2. This is due to the amino terminals of the polymer particle causing an intraparticle but interchain PET from the primary amino groups to the fluorophore aided by its cationic side-chain.

pH dependence of absorbance can also be subjected to Henderson-Hasselbalch analysis to yield pK_a values in cases concerning homogeneous solutions. Close agreement is found with the corresponding pK_a* values. Owing to the separation of the H^+ receptor from the fluorophore and the lack of a significant dipole in the excited state of **19**,[24, 34] the following equation (2) usually holds (Table 1).

$$pK_a = pK_a^* \qquad (2)$$

This is also true for **8**, in spite of its excited state dipole of 11D,[24] suggesting that the fluorophore-receptor separation is the major cause of equation (2).

Some complications which occurred during this study need to be noted and lessons learned. YES logic-tagged APEG-PS particles **9** display the expected H^+-induced fluorescence switching 'on', but leaching of fluorescent species occurs in mixed aqueous solutions over a period of several hours. Eventually the tags are lost. This behaviour can be ascribed to the hydrolysis of the amide bond anchoring the tag, catalyzed by the exposed tertiary amine nucleophile of an adjacent tag.[35] Such action is facilitated by the long, flexible and rather hydrophilic PEG chains. The APS counterpart **10** is stable under similar conditions because of the shortness of the hydrophobic propyl chain. We also note that the APEG-PS based **3** is stable because its non-terminal tertiary amine unit is flanked by the bulky anthracene fluorophore so that its nucleophilicity is suppressed. The stability of **3** also provides evidence that terminal primary amines of APEG-PS do not contribute to nucleophilic catalysis of tag hydrolysis.

PASS 1 logic-tagged APS particles **12** display weak emission, presumably due to the surface Si-OH/Si-O^- causing intraparticle hydrogen bonding with the excited fluorophore. Related fluorescence quenching due to intramolecular hydrogen bonding is known.[24] This problem was solved by employing a more hydrophilic version of **12**, **15**, so that the better solvation of the ICT fluorophore takes it to an average position which is further from the surface groups and closer to the bulk liquid. Intraparticle hydrogen bonding-based quenching effects on ICT excited states by surface Si-OH/Si-O^- could also have occurred in the case of YES-tagged material **10**. However, such issues were not visible at basic pH since intramolecular PET-based quenching within the aminoethylaminonaphthalimide moiety is faster. Similarly, no intraparticle quenching by Si-OH is seen at acidic pH because the hydrophilic protonated receptor pulls the fluorophore away from the APS surface towards the bulk liquid.

Table 2. Ideal logic table for a H^+-driven (YES + PASS 1) logic gate with fluorescence output. The fluorescence intensities from two binary logic gates are observed as a sum total.

	YES	PASS 1	(YES + PASS 1)
Input $[H^+]$	Output Fluorescence	Output Fluorescence	Output Summed Fluorescence
0	0	1	1
1	1	1	2

Table 3. Observed logic table for H^+-driven (YES + PASS 1) logic gates **17** and **18** with fluorescence output, measured as the total emission from both logic components in each case.

Input $[H^+]$	**17** Output Fluorescence λ_{ex} 368 nm, λ_{em} 422 nm	**18** Output Fluorescence λ_{ex} 429 nm, λ_{em} 530 nm
0 (10^{-11} M)	$1.0^{a,b}$	$1.0^{a,c}$
1 ($10^{-2.5}$ M)	2.0^{b}	1.5^{c}

a; Normalized value, b; Observed pK_a^* = 5.2, b; Observed pK_a^* = 9.8

These complications are avoided by **18**, where **8** and **16** are used to double-tag APS. The same holds true for **17**, where **1** and **2** are the two tags on APS and for **21**,[8] where **1** and **2** are the two tags on APEG-PS. As mentioned earlier,[8] double-tagging leads to significant strengthening of the MCID approach by increasing the number of distinguishable objects. The physical electronic representation of the (YES + PASS 1) logic case is illustrated in Figure 7 and the ideal logic table is given in Table 2. Table 3 gives the observed behaviour of **18** and **17**. The FE_{H+} value for **17** is the ideal value of 2.0 while that for **18** is 1.5. The lower value seen for **18** is because its I_{Fmin} value is measured at pH 11.0 which is not far enough away from the pK_a^* value of 9.8. Fluorescence measurements on 4-aminonaphthalimides at pH > 11.0 are not suitable for PASS 1 logic behaviour, due to excited state deprotonation.[24] Another indication of ideal (YES + PASS 1) logic behaviour is found in the measured pK_a^* value in each case being essentially identical to the corresponding value for the case tagged with YES logic alone.

Conclusion

Molecular logic identification tags emitting blue and green have been synthesized and evaluated on organic and inorganic polymer particles. H^+-controlled fluorescence switching abilities of the logic tags are translatable to polymer particle surfaces, in spite of the lower polarities of these surfaces. The approach of employing tertiary amines as H^+ receptors on H^+-driven YES logic tags works well, as long as rather nucleophilic terminal amines are not combined with long, flexible and rather hydrophilic linkers on the particle surface. Some degree of hydrophilicity is also necessary for H^+-driven PASS 1 logic tags of the ICT type to be strongly emissive on APS surfaces. Pure $\pi\pi^*$-based PASS 1 tags function well even when they are rather hydrophobic. Once the above caveats are respected, ternary logic tags of the (YES + PASS 1) type are successfully demonstrated. Further extensions of molecular computational identification to other emission colours, other logic types,[22] and other objects are awaited.

Experimental section

See supporting information for detailed synthetic procedures and for pH-dependent fluorescence spectra of **9** and **10**.

Acknowledgements

We thank the European Social Fund, IAESTE and the Department of Employment and Learning, Northern Ireland.

Keywords: molecular logic • molecular computation • molecular computational identification • photoinduced electron transfer (PET) • fluorescent PET switches

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